

## Claims

1. A process for the preparation of a polymeric alkoxyamine by atom transfer radical addition polymerization (ATRA) comprising the following steps

- a) reacting a mono nitroxide of formula (A)  $X-Ln-NO\bullet$  (A); or
- b) reacting a bis nitroxide of formula (B)  $\bullet ON-Ln-NO\bullet$  (B) with a bis-functional compound of formula (C)  $X-Lh-X$  (C); or
- c) reacting a polynitroxide of formula (D)  $Ln-[NO\bullet]_n$  (D) with a poly-functional compound of formula (E)  $Lh-[X]_n$  (E);

in the presence of a transition metal or transition metal salt in its lower oxidation state and optionally a ligand, capable of complexing the transition metal or transition metal salt;

wherein

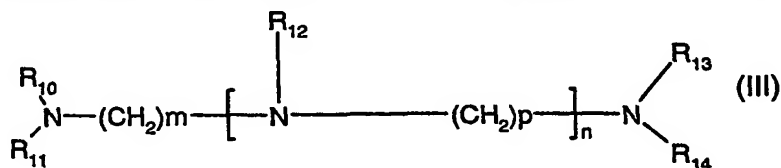
X is halogen or -SCN;

$Ln$  is a  $n$  valent spacer group connecting the nitroxide group with the group X or with the other nitroxide groups;

$Lh$  is a  $n$  valent spacer group connecting the groups X

$n$  is a number from 3 to 6.

2. A process according to claim 1 wherein the ligand is of formula III



wherein  $R_{10}$ ,  $R_{11}$ ,  $R_{13}$  and  $R_{14}$  are independently H,  $C_1$ - $C_{12}$ alkyl,  $C_5$ - $C_{12}$ cycloalkyl or aryl;

$R_{12}$  is H,  $C_1$ - $C_{12}$ alkyl,  $C_5$ - $C_{12}$ cycloalkyl or aryl or a group  $-(CH_2)_q-NR_{10}R_{11}$ ;

$m, p$  and  $q$  are numbers from 1-4;

$n$  is a number from 0 to 4; or

the ligand is a bicyclic or polycyclic heteroaliphatic ring.

3. A process according to claim 1 wherein the ligand is selected from the group consisting of tris[2-(dimethylamino)ethyl]amine, N,N,N',N',N''-pentamethyldiethylenetriamine, N,N,N',N'-tetramethylethylenediamine, 1,1,4,7,10,10-hexamethyltriethylenetetramine, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,5,9-trimethyl-1,5,9-triazacyclododecane, 1,4,8,11-tetramethyl-

1,4,8,11-tetraazacyclotetradecane, 2,2'-bipyridyl, 2,2'-bi(4-*t*-butyl)pyridyl and 2,2',2''-terpyridyl.

4. A process according to claim 1 wherein the molar ratio between the transition metal or transition metal salt in its lower oxidation state and the halogen or -SCN containing compound is from 1:1 to 1:3.

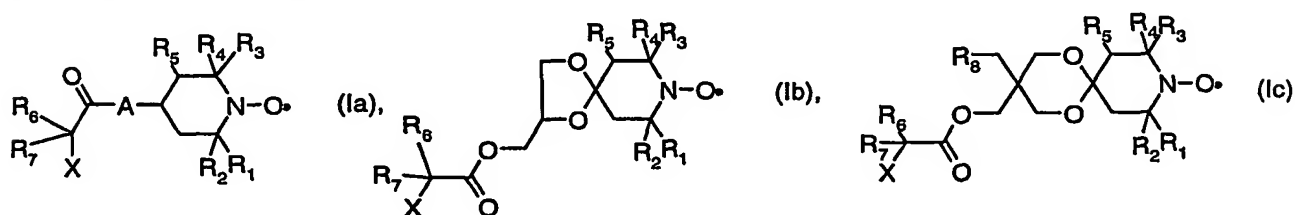
5. A process according to claim 1 wherein the transition metal is selected from the group consisting of Cu, Fe, Mn, Mo, Cr, Ni and Ru and the transition metal salt in its lower oxidation state is a halogenide, sulfate, nitrate, carboxylate or trifluormethane sulfonate of these metals.

6. A process according to claim 1 wherein the molar ratio between the ligand and the transition metal or transition metal salt in its lower oxidation state is from 0.5:1 to 1:5.

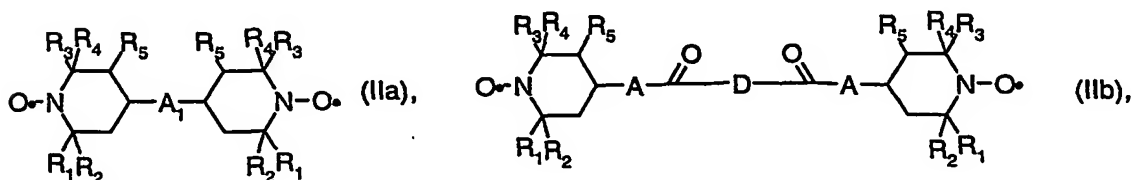
7. A process according to claim 1 wherein the polymerization temperature is from -20°C to 100°C.

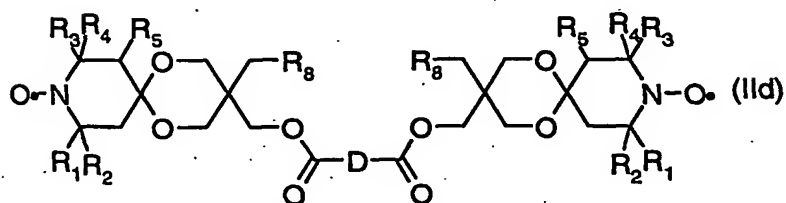
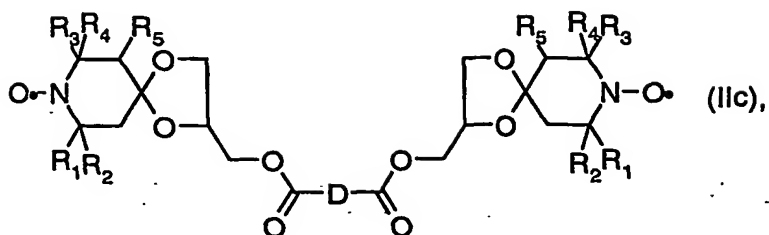
8. A process according to claim 1 wherein

a) the mono nitroxide of formula (A) is of formula (Ia), (Ib) or (Ic)

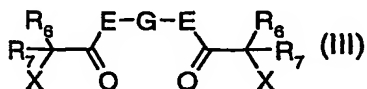


b) the dinitroxide of formula (B) is of formula (IIa), (IIb), (IIc) or (IId)

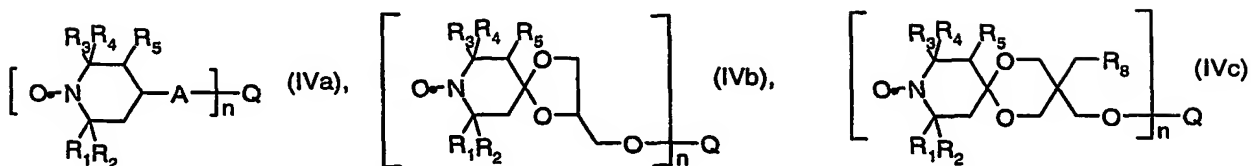




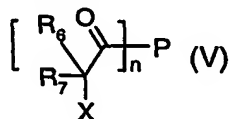
the compound of formula (C) is of formula (III)



c) the polynitroxide of formula D is of formula (IVa), (IVb) or (IVc)



the compound of formula (E) is of formula (V)



wherein in the formulas

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are methyl or ethyl; or

$R_1$  and  $R_2$  and/or  $R_3$  and  $R_4$  together with the carbon atom to which they are bonded form a  $C_5$ - $C_8$ cycloalkylring;

$R_5$  is H or methyl;

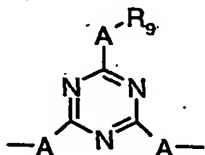
$R_6$  and  $R_7$  are H,  $C_1$ - $C_8$ -alkyl or aryl;

$R_8$  is H or methyl;

X is halogen or  $-\text{SCN}$ ;

A is O or  $\text{NR}_9$  wherein  $R_9$  is H or  $\text{C}_1\text{-C}_{18}$ alkyl,  $\text{C}_5\text{-C}_{12}$ cycloalkyl or aryl;

$A_1$  is a group  $-\text{NR}_9\text{-(CH}_2\text{)}_a\text{-NR}_9\text{-}$  wherein a is a number from 2 to 12 or a group



D is a direct bond or  $\text{C}_1\text{-C}_{12}$ alkylene,  $\text{C}_5\text{-C}_{12}$ cycloalkylene or arylene, wherein the alkylene and cycloalkylene may be interrupted by one or more O, S or N atoms;

E is a direct bond, O or  $\text{NR}_9$ ;

G is  $\text{C}_1\text{-C}_{12}$ alkylene,  $\text{C}_5\text{-C}_{12}$ cycloalkylene or arylene wherein the alkylene and cycloalkylene may be interrupted by one or more O, S or N atoms;

n is 3 or 4;

Q is the acyl residue of a trivalent or tetravalent carboxylic acid;

P is the residue of a trivalent or tetravalent alcohol.

9. A process according to claim 8 wherein the compound is of formula (Ia), (Ib) or (Ic).

10. A process according to claim 9 wherein the compound is of formula (Ia), (Ib) or (Ic);

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are methyl;

$R_5$  is H;

$R_6$  and  $R_7$  are independently H or methyl;

$R_8$  is H or methyl;

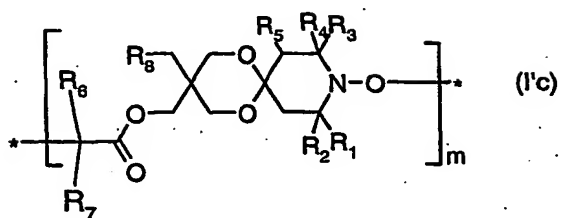
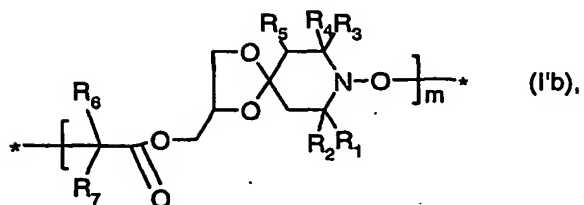
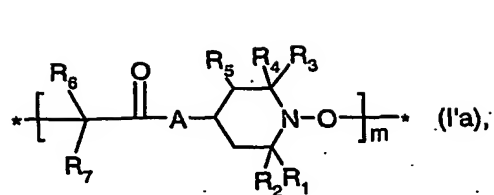
X is Cl or Br;

A is O or  $\text{NR}_9$  and  $R_9$  is H or  $\text{C}_1\text{-C}_{18}$ alkyl.

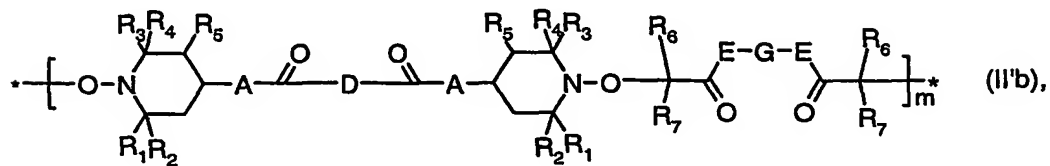
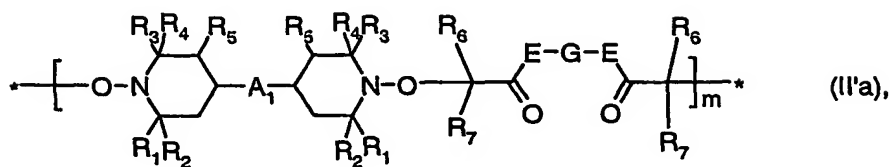
11. A process according to claim 10 wherein the compound is of formula (Ia).

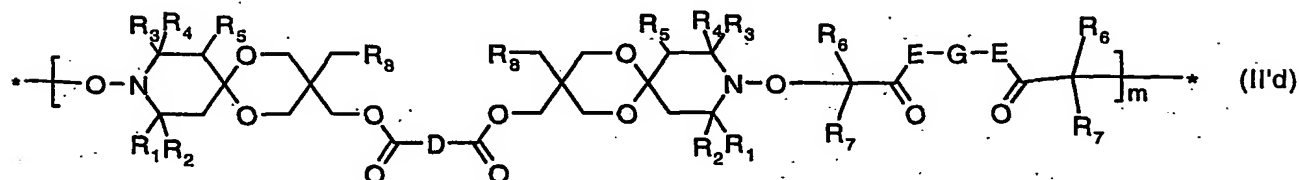
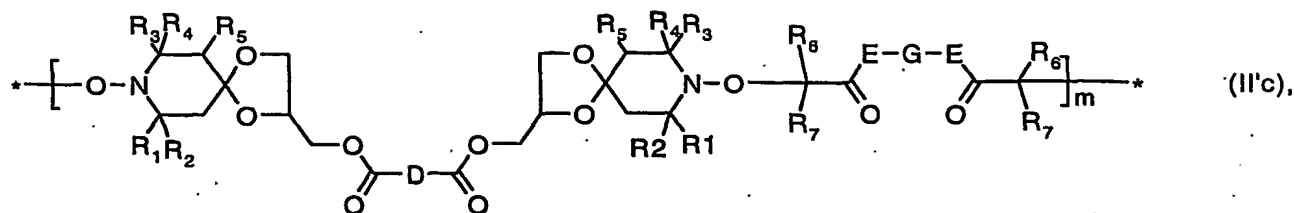
12. A polymer obtainable by a process according to claim 1

13. A polymer with a repetitive structural element of formula (I'a), (I'b), (I'c)



(II'a), (II'b), (II'c) or (II'd)





wherein in the formulas

m is a number from 1 to 5000

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are methyl or ethyl; or

R<sub>1</sub> and R<sub>2</sub> and/or R<sub>3</sub> and R<sub>4</sub> together with the carbon atom to which they are bonded form a C<sub>5</sub>-C<sub>8</sub>cycloalkyl ring;

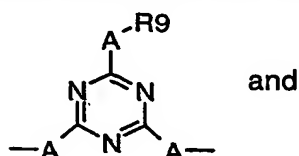
R<sub>5</sub> is H or methyl;

R<sub>6</sub> and R<sub>7</sub> are H, C<sub>1</sub>-C<sub>8</sub>-alkyl or aryl;

R<sub>8</sub> is H or methyl;

A is O or NR<sub>9</sub> wherein R<sub>9</sub> is H or C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl or aryl;

A<sub>1</sub> is a group -NR<sub>9</sub>-(CH<sub>2</sub>)<sub>a</sub>-NR<sub>9</sub>- wherein a is a number from 2 to 12 or a group

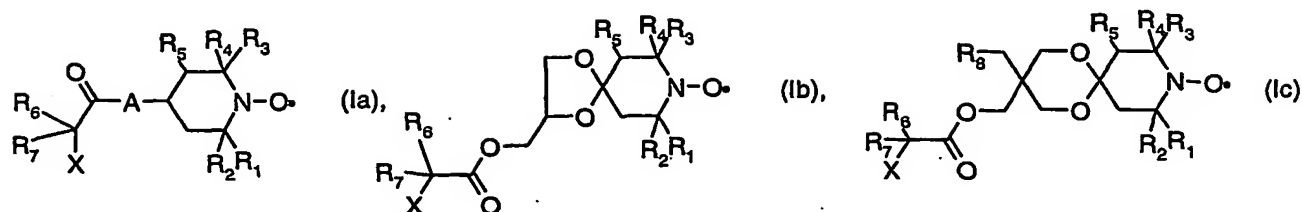


D is a direct bond or C<sub>1</sub>-C<sub>12</sub>alkylene, C<sub>5</sub>-C<sub>12</sub>cycloalkylene or arylene, wherein the alkylene and cycloalkylene may be interrupted by one or more O, S or N atoms;

E is a direct bond, O or NR<sub>9</sub>; and

G is C<sub>1</sub>-C<sub>12</sub>alkylene, C<sub>5</sub>-C<sub>12</sub>cycloalkylene or arylene wherein the alkylene and cycloalkylene may be interrupted by one or more O, S or N atoms.

14. A compound of formulae (Ia), (Ib) or (Ic)



wherein in the formulas

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are methyl or ethyl; or

R<sub>1</sub> and R<sub>2</sub> and/or R<sub>3</sub> and R<sub>4</sub> together with the carbon atom to which they are bonded form a C<sub>5</sub>-C<sub>8</sub>cycloalkylring;

R<sub>5</sub> is H or methyl;

R<sub>6</sub> and R<sub>7</sub> are H, C<sub>1</sub>-C<sub>8</sub>-alkyl or aryl;

R<sub>8</sub> is H or methyl;

X is halogen or -SCN;

A is O or NR<sub>9</sub> wherein R<sub>9</sub> is H or C<sub>1</sub>-C<sub>18</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl or aryl.

15. A stabilized composition, which comprises

(a) an organic material subject to degradation by heat, light or oxygen, and

a compound obtained by a process according to claim 1.

16. A composition according to claim 15 wherein component (a) is a natural or synthetic polymer.

17. A composition according to claim 15 which additionally contains at least one coadditive stabilizer selected from the group consisting of the phenolic antioxidants, metal stearates, metal oxides, organophosphorus compounds, furanone antioxidants, hydroxylamines, UV absorbers, hindered amines stabilizer different from that obtained according to the process of claim 1 and mixtures thereof.

18. Use of a polymer obtainable by a process according to claim 1 as stabilizer for natural or synthetic polymers.

19. Use of a polymer obtainable by a process according to claim 1 as flame retardant additive in natural or synthetic polymers.

20. Use of a polymer obtainable by a process according to claim 1 as polymerization initiator/regulator in controlled radical polymerization reactions.